

least one layer consisting of Group IVB-VIB metals, a mixture thereof or substitution alloys, at least one layer consisting of solutions of nonmetal atoms of nitrogen, carbon, boron in said metals, at least one layer of chemical compounds of said metals with nonmetals in the form of nitrides, carbides, borides and mixtures thereof, implanted in at least one of any of said layers high-energy non metal ions selected from the group consisting of argon, nitrogen, carbon or boron ions.

A marked-up copy of prior pending claims 16-17 and 19-28 showing the changes made is attached hereto as Exhibit C.

#### REMARKS

Reconsideration and withdrawal of the Examiner's rejection of the above-identified application is respectfully requested in view of the foregoing amendments and following remarks. Claims 16-30 are in the application. Claims 16-17 and 19-28 have been amended. The specification has been amended. No new matter has been added.

The Examiner objected to the specification for some typographical errors. Applicant has amended the specification accordingly and submits a substitute specification. No new matter has been added.

The Examiner rejected claim 24 under 35 U.S.C. §112, first paragraph. Applicant has corrected the typographical errors in claim 24 to overcome this rejection.

The Examiner rejected claims 16-30 under 35 U.S.C. §112, second paragraph. Applicant has amended claims 16-17 and 18-28 to further clarify the invention. Regarding the term "vibromechanical treatment", Applicant submits that vibromechanical treatment is applied in the present invention in order to create more favorable relations between residual stresses in the surface layers of coated parts and in the coating itself and to provide better quality of the whole system (the part and the coating) by reducing roughness of the surface. The essence of vibromechanical treatment is that the coated part should be placed in a metal container supported by spring or hydraulic suspensions with an electric drive on a crank engine. By vibration, such treatment with micropellets is conducted on the surface and the stress condition changes in the surface layers. Applicant submits that this term is known in the art and is sufficiently clear.

The Examiner rejected claims 28-30 as being anticipated by *Kerber* and rejected claims 16, 18-21, 23-24 and 26-27 as being unpatentable over *Kerber* in view of *Suzuki et al.* and *Dearnaley*.

Claims 22 and 25 are rejected over *Kerber* in view of *Suzuki et al.* and further in view of *Engel*. Applicant respectfully traverses.

*Kerber* teaches about multilayer coatings comprising metallic and ceramic layers of oxides, carbides and nitrides of titanium and zirconium and can indeed be applied for coatings on steam turbine blades made of steel under the conditions of erosion, corrosion, stress, fatigue and creep (page 3 of the description of invention). However, there are no data in the patent, except only very generally, that would properly cover the properties that the coatings impart to the blades. The present invention is based on the measured effects that the claimed method for coating deposition provides, and the structure of the coating is substantiated by these improved properties.

*Kerber* teaches about coatings formed of a plurality of alternating layers of ceramic and metallic materials (i.e. basically two alternating layers) and transition zones which are formed always in the course of many-layer coating deposition from plasma as one gaseous atmosphere is gradually changed by another, and as this occurs, the transition areas are not regulated by any means.

The present invention requires at least three layers to be formed and, which is important, each layer should have a certain thickness and should be formed as a result of the gradual and controlled changing in the composition of gaseous atmosphere. Kerber states that layers of metallic materials should be thicker (about 4 times as thick) as compared to the ceramics. For instance, with the metallic layer of 2 microns, the ceramics layer is 0.5 microns, (claims 3,8,12,15 in the Kerber patent). These thickness ratios would not provide erosion and corrosion characteristics of aircraft compressor turbine blades and vanes, nor would they impart the necessary mechanical properties.

Therefore, contrary to Kerber, the present invention claims 3 or 4 layers (the fourth layer being a rare metal sublayer or scandium in case additional adhesion to the basic material is required), and the certain thickness ratios, which should be 1:2:2.5 (claim 6), and the layer compositions (see page 5 of the invention description and claims 5, 8 of the application), which are provided by certain changes in the gaseous atmosphere. Among other things, the present application claims deposition of mixtures or alloys of metals, for instance, titanium and zirconium, or zirconium and molybdenum or other metals selected from transitional elements that, as compared to pure metals, have different hardness

characteristics, linear expansion coefficients and mechanical properties.

Composition of the metallic layers changes according to certain laws (see, for instance, Fig.3), which is defined by the deposition conditions, i.e. the rate at which pressure changes in the vacuum chamber, the number and composition of cathodes, the table rotation speed and other technology parameters. That makes it possible to considerably increase durability of coated parts by attaining a whole set of characteristics: the wear resistance, retention of mechanical properties at the required level, high adhesion of the coating to the surface of coated parts and sufficient relations between the coefficients of linear expansion of the part and the coating.

One of the major distinctions of the claimed technology is that the ion implantation takes place directly (i.e. simultaneously with the interstitial phase formation) in the course of coating deposition from plasma. In order to make it feasible, the coating machine is equipped with an additional ion source (the ion implanter), which can operate as the deposition process is going on and, which is important, the energy of ions changes considerably, which causes the effects of superstructure changes (which is true also for the nitrides, carbides and borides) thus providing the extremely high level of wear resistance. (See Fig. 4).

It is known (Goldsmit H.J., 1967, Interstitial Alloys, Butterworths, London) that interstitial alloys are phases with the crystal lattice of NaCl type characterized with a certain homogeneity region, i.e.  $\text{TiN}_{1.2...0.38}$  ,  $\text{TiC}_{1.0...0.28}$  ,  $\text{ZrC}_{1.0...0.28}$  .  $\text{ZrN}_{1.0...0.55}$ , and therefore ion implantation should be carried out immediately as such phases are being formed in order to create new compounds of phases oversaturated with interstitial atoms (see Fig. 2 in the application). These compounds were at first suggested to possess and then indeed found to possess better characteristics of wear resistance, and such compounds (see, for instance, phases shown in Fig.2 of the application) can not be formed in the conditions of coating deposition as described in the cited patents. We have not read that such approach be used in any of the published materials we found available (including the references cited by the respected Examiner such as Suzuki, Dearnely, etc.). In all the patents and publications devoted to ion-assisted coating deposition, including the patents cited by the Examiner, the ion implantation is employed after the coating has been deposited, even if an implantor is located in the same chamber with the plasma source, as the role of implantor in those cases is to improve adhesion of the layers deposited or to mix a non-metal into the metal layer after the coating has been formed. Suzuki teaches that ion plated films are characterized with stronger bonds to the substrate as compared to the vacuum-deposited films, i.e. he

teaches about adhesion. And implantation with nonmetal ions is meant to produce nitrides, i.e. not simultaneously with but after the coating has been deposited.

In the present application, however, implantation is employed to modify the properties of coating layers themselves and of the coating system as a whole rather than to improve adhesion. Adhesion can be and is also improved, but the invention relies on the functioning of sublayers of scandium or rare metals to attain better adhesion.

In order to solve the problem of combining implantation with ion plasma deposition the coating machine is equipped with a source of ions with the energy of up to 50 kV and a large diameter beam, which can not be otherwise provided by other ion sources.

*Dearnely* teaches about hardness being improved as such compounds as nitrides, borides and carbides are formed on the steel surface. It should be noted that the cited patents are relevant for wear resistant tool materials and so they do not take into account the set of coating properties required for wear resistance in the conditions of gaseous abrasive flows, when it is necessary to retain a certain level of mechanical properties and a certain quality of the surface.


Accordingly, Applicant submits that claims 16-30 are patentable over the prior art, taken either singly or in combination. Early allowance of the amended claims is respectfully requested.

Respectfully submitted,  
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Enclosure: Exhibits A, B and C

  
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I hereby certify that this correspondence is being deposited with the U.S. Postal Service as first class mail in an envelope addressed to: Assistant Commissioner of Patents, Washington, D.C. 20231, on December 27, 2002.

  
Maria Guastella





EXHIBIT C

MARKED-UP VERSIONS OF CLAIMS 16-17 AND 19-28

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16. (Amended) A method for depositing wear-resistant coatings on metal surfaces of machine components and articles, said method comprising the following steps:

- (i) providing an ion-plasma deposition chamber;
- (ii) locating as an anode said machine components or articles being treated inside said ion-plasma deposition chamber; <sup>[as an anode]</sup>
- (iii) locating in said chamber cathodes made from <sup>^</sup>the Group IVA-VIA metals and/or alloys thereof;
- (iv) establishing in said chamber a gas atmosphere wherein the gas is selected from the group consisting of inert or non-inert gases and mixtures thereof;
- (v) effecting, whenever necessary, ion cleaning of surfaces of said machine components or articles;
- (vi) effecting selective ion-plasma deposition of layers of a coating, wherein at least one layer (a) consists of said metals, mixtures thereof or substitution alloys, a second layer (b) consists of solutions of nonmetallic atoms of nitrogen, carbon, and boron in said metals, and a third layer (c) consists of chemical compounds of said metals with nonmetals in the form of nitrides, carbides, borides and mixtures thereof;
- (vii) subjecting one or more of said layers to treatments by implanting thereinto [high energy] non-metallic ions;
- (viii) cooling and unloading said machine components or articles from said chamber.

17. (Amended) A method as claimed in claim 16, characterized in that after having been cooled and unloaded said machine components or articles are subjected to vibromechanical treatment with [micropellets] pellets.

19. (Amended) A method as defined in claim 16, wherein said cathodes are [selected from] titanium alloys[, steels or nickel-based alloys] which after deposition form a composition similar to the base material of a machine component or article.

20. (Amended) A method as defined in claim 16, wherein there are from 3-500 layers [said plurality of microlayers is selected from the numbers 3-500], and said [microlayers] layers (a), (b), (c) alternate successively.

21. (Amended) A method as defined in claim 19, wherein the [thickness values of said microlayers] layers (a), (b), (c) are in a thickness ratio of 1.0:2.0:2.5.

22. (Amended) A method as defined in claim 16, further comprising the step of [preliminary deposition of a microlayer] depositing a first layer consisting of scandium, yttrium or other rare earth metal having a thickness of 0.02 to 0.08 micron before step (vi).

23. (Amended) A method as defined in claim 16, wherein the [reaction] gas atmosphere is nitrogen, acetylene, methane or diborane.

24. (Amended) A method as defined in claim 16, wherein said step of ion deposition is effected with ions of argon, or nitrogen, or carbon, or boron at an accelerating voltage of 10-50 kV, at a radiation dose of [10<sup>14</sup>-10<sup>18</sup>] 10<sup>14</sup> - 10<sup>18</sup> ion/sq.cm. and an energy of ions of [5x10<sup>3</sup> - 1x10<sup>5</sup>] 5 x 10<sup>3</sup> - 1 x 10<sup>5</sup> eV.

25. (Amended) A method as defined in claim 16, wherein said ion-plasma deposition step (vi) comprises the steps of depositing:  
(a) a scandium [microlayer] layer in an argon atmosphere;  
(b) a titanium [microlayer] layer in an argon atmosphere;

(c) a [microlayer] layer comprising a solid solution of implanted nitrogen ions in titanium in an atmosphere comprising a mixture of nitrogen and argon;

(d) a [microlayer] layer comprising titanium nitride implanted with nitrogen ions in nitrogen atmosphere [.] ;

(e) a zirconium [microlayer] layer in argon atmosphere;

(f) a [microlayer] layer comprising a solid solution of implanted nitrogen ions in zirconium in an atmosphere comprising a mixture of nitrogen and argon;

(g) a [microlayer] layer comprising zirconium nitride implanted with nitrogen ions in nitrogen atmosphere; and

(h) the step of repeating said steps (b-g) in that order to provide [the required plurality of microlayers] a desired number of layers.

26. (Amended) A method as defined in claim 16, wherein said deposition step (vi) comprises depositing:

(a) a first [microlayer] layer comprising alloys of titanium and zirconium in an inert gas atmosphere;

(b) a [microlayer] layer comprising alloys of titanium and zirconium implanted with nitrogen atoms in an atmosphere of a mixture of said inert gas and nitrogen;

(c) a [microlayer] layer comprising titanium and zirconium nitrides implanted with nitrogen ions in nitrogen atmosphere;

(d) repeating said steps (a) -(c) to provide [the required plurality of microlayers] a desired number of layers to form a multilayer coating; and

(e) [ion deposition with] implanting argon ions [of] in the [deposited] multilayer coating.

27. (Amended) A method as defined in claim 26, wherein said deposition step (vi) comprises depositing:

(a) a [microlayer] layer of titanium and zirconium alloys in an inert gas;

(b) alloys of titanium and zirconium with boron in a mixture of an inert gas with diborane;

(c) titanium and zirconium borides implanted with boron;

(d) repeating said steps (a)-(b) in that order to provide [the required plurality of microlayers] a desired number or layers to form a multilayer coating; and

(e) [ion implantation with] implanting argon ions in the multilayer coating [deposited].

28. (Amended) A [wear-resistant] coating of metal surfaces, comprising deposited on said surfaces by ion-plasma deposition process at least one [microlayer] layer consisting of Group [IVA-VIA] IVB-VIB metals, [their] a mixture thereof or substitution alloys, at least one [microlayer] layer consisting of solutions of nonmetal atoms of nitrogen, carbon, boron in said metals, at least one [microlayer] layer of chemical compounds of said metals with nonmetals in the form of nitrides, carbides, borides and mixtures thereof, implanted in at least one of any of said [microlayers] layers high-energy non metal ions selected from the group consisting of argon, nitrogen, carbon or boron ions.



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EXHIBIT A

5      **Method for Deposition of Wear Resistant Coatings to Improve Service Life of  
Coated Components**

Field of the Invention

10      This invention relates to metallurgy and machine building fields and more specifically to development of methods that improve service life and durability of machine components; to repair of components and reconstitution of their properties; and particularly to gas turbine blades and vanes; and primarily to coatings applied to metal surfaces of aircraft engine compressor blades and vanes.

15      Background of the Invention

20      Frequently, aircraft and helicopters equipped with gas-turbine engines have to operate under conditions of considerable dust content in the air flow and high humidity of sea environment with aggressive elements of corrosive effects. These operation conditions result in abrasion-caused erosion and corrosion of aircraft parts, particularly the compressor blades. Under these conditions, geometry of blades is distorted, operating performances are deteriorated, fuel consumption increases, and engine maintenance and repair expenses grow considerably. The said deteriorating processes can not be efficiently avoided by installation of dust protective devices.

25      Eroded blades and vanes are generally restored by edge profile polishing or are replaced with new blades and vanes. Such blades and vanes are made of titanium-based alloys or high-alloy steels, which are expensive and difficult to process, so engine repair entails great expense.

30      U.S. Patent No.4,904,542, issued February 27, 1990, reissued under Re.34,173 on February 2, 1993, to Midwest Research Technologies Inc. describes a coating formed of a plurality of alternating layers of metallic and ceramic materials. The two materials selected for the layers have complementary wear resistant characteristics such that one is relatively ductile and the other is relatively hard and brittle.  
35      Preferably radio-frequency sputtering is employed to deposit the coating, since it does not produce excessive heating which could negate any prior heat treatment of the substrate onto which the coating is deposited.



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5 Also known are RU Patents No.2,061,090 BI No. 15, 1996 and No.2,106,429 BI No. 7, 1998, that describe methods of multi-layer coating deposition on parts and tools, including transition metal coatings. Zirconium is offered as an adhesive bondcoat that is applied to the substrate before the coating; or there is an alternative method of applying metal oxides between the metal layers.

10 A deposition technique is also known to produce thin films of  $CN_x$  with implantation of nitrogen ions from plasma. U.S. Patent No. 5,580,429 issued December 3, 1996, to Northeastern University describes cathodic/anodic vacuum arc sources with a plasma ion implantation deposition system for depositing high quality thin film coatings on substrates. Both cathodic and anodic vacuum arc deposition  
15 sources, CAVAD, are used to create a plasma vapor from solid materials composing the cathode and/or anode in the cathodic and/or anodic arc, respectively. Gases, e.g., hydrogen or nitrogen can be in the deposited films by creating a background plasma of the desired gas using either RF energy, thermionic emission, or consequential ionization of the gas passing through the arc or around the substrate. Highly negative  
20 pulses are applied to the substrate to extract the ions and provide them with the appropriate energy to interact with the other species in the thin film formation on the substrate to form the desired films. The substrate is bombarded with ionized particles to form carbon nitrides with variable  $[N]/[C]$  ratios.

RU Patent No.2,062,818 issued June 27, 1996, describes deposition of metal-  
25 containing coatings on large substrates in vacuum. The method includes inert gas ion beam cleaning of the substrate and metal-coating deposition by cathodic sputtering in the inert gas discharge when the substrate is bombarded with the inert gas ion beam that is formed by an accelerator of closed-type drift of electrons at an inert gas ion energy of 50-150 eV. Technically, this method is the closest one to the present  
30 invention.

However, the aforesaid U.S.P. 4,904,542, U.S.P. 5,580,429 and R.U. 2,062,818, R.U. 2,061,090, and R.U. 2,106,429 do not fully cover the problems of durability and wear resistance, especially as far as aircraft engine blade airfoil surfaces are concerned, which must meet various specific requirements to their wear  
35 and corrosion resistance properties and at the same time retain a certain level of their mechanical and, particularly, fatigue characteristics.

Therefore, there is a need to provide improved erosion and corrosion resistance and, as a result, improved reliability and durability of components of

5 various machines, tools and equipment, especially gas turbine engine compressor blades and vanes. That is proposed to be achieved by vacuum plasma technology involving ion implantation.

### Summary of the Invention

10

It is an object of the present invention to provide a technique of coating deposition on metal surfaces, particularly on components of machines, steam and gas turbines, and even more specifically on aircraft engine compressor blades and vanes, that will ensure improved erosion and corrosion resistance and retain the sufficient  
15 level of mechanical properties, primarily, fatigue characteristics.

It is a further object to restore the metallic surface of an eroded or corroded metal substrate, particularly the profile surface of a working blade of a gas turbine engine compressor to its original geometric shape and profile parameters.

To achieve the aforementioned objects, a coating is deposited that consists of  
20 at least three or four microlayers with certain thickness and compositions. By the term "microlayer", in this specification and claims, is meant a layer of pure metal, multiple-component substitution or interstitial metal alloy with non-metal atoms, or interstitial phases based on the said metals, i.e. the metal carbides, nitrides, borides, or complex compounds of the said phases, e.g., carbonitrides, carboborides, etc..

25 The said coating is produced by means of ion plasma deposition; in the preferred embodiments, the said coating consists of a special microlayer (hereinafter referred to as "submicrolayer"); the said submicrolayer is a rare earth metal, particularly scandium, yttrium or lanthanum and lanthanoids; the said coating also comprises a plurality of microlayers wherein each of said microlayers comprises a  
30 material selected from the group consisting of the Group IVB-VIB (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) or alloys thereof, interstitial solid solutions of elements (carbon, nitrogen, boron), nitrides, carbides, or borides of metals, wherein one or more of said microlayers has been subjected to high energy non-metallic (argon, nitrogen, carbon, boron) ion deposition.

35 The said microlayers of metals or said alloys or metal/non-metal compounds deposited by means of deposition of ions or neutral particles under an appropriate inert gas or non-inert gas, such as nitrogen, methane, acetylene, diborane, should be deposited to a desired thickness, preferably 0.1-10 microns.



5       The microlayer may be an essentially discrete layer distinct from the adjacent  
 substrate or microlayers; or it may be a mixture therewith. Each of the microlayers  
 may comprise a pure metal or an alloy thereof as prepared, for example, if more than  
 one metallic cathode are simultaneously activated within the chamber or the cathodes  
 are made of alloys. The order of the plurality of microlayers can be selected by opting  
 10 between corresponding gas atmospheres in the working chamber and by activating the  
 appropriate cathode(s). The number and order of microlayers constituting the full  
 coating and the inert or non-inert gas ions deposition can be selected depending on  
 the specific requirements determined by the desired performances of machine parts or  
 the whole machine. For example, it is essential that guide blades of the aircraft engine  
 15 compressor had very hard and wear resistant surfaces, and at the same time fatigue  
 characteristics of the substrate alloy would not play a restrictive role, since such  
 blades are not subjected to high fatigue. On the contrary, working blades of the  
 compressor are very sensitive to fatigue conditions as such blades have to operate  
 under considerable fatigue stresses. Therefore, coatings designed for guide and  
 20 working blades differ in their thickness and number of microlayers.

The method claimed involves deposition of, at least, three functional microlayers:

1 - a damping, corrosion-resistant microlayer of a rare earth metal from the  
 Groups IVB - VIB or a replacement alloy based on said metals, deposited in inert gas  
 25 atmosphere to the desired thickness, preferably 0.02 - 5 microns, that provides  
 relaxation of erosion-caused stresses between solid layers and protects from  
 corrosion-aggressive agents of media;

2 - a reinforcing microlayer consisting of interstitial solid solutions of  
 nitrogen, boron, carbon in transition metals of the second layer, deposited to the  
 30 desired thickness, preferably 0.04 - 10 microns, in a non-inert gas (nitrogen, diborane,  
 methane, or acetylene, respectively, at a partial pressure of said gases  $0.05 - 5 \times 10^{-1}$  Pa)  
 atmosphere, that provides a gradual transition to a high strength layer;

3 - a wear-resistant, high strength microlayer consisting of interstitial phases  
 such as nitrides, borides, carbides or complex compounds thereof based on said  
 35 transition metals, deposited to the desired thickness, preferably 0.1 - 12.5 microns, in  
 corresponding non-inert gas atmospheres at a partial pressure of  $0.1 - 5 \times 10^{-1}$  Pa, that  
 provides resistance to erosion effects of abrasive particles.

5 The deposition of the aforementioned functional microlayers is carried out by activating the appropriate cathode made of a pure metal or a multiple-component alloy, by selecting the necessary partial pressure and composition of the gas atmosphere, and by controlling the appropriate time of deposition as required.

Fig. 1 shows an exemplary microstructure of the claimed coating on an aircraft engine compressor blade of titanium alloy.

Simultaneously, one or more microlayers is subjected to non-metallic (argon, nitrogen, carbon or boron) ion treatment by means of an ion implantor; it is important that such treatment must be carried out directly in the working chamber of the ion-plasma device, simultaneously with or immediately following the deposition process. The ion treatment is carried out with ions at  $5 \times 10^3 - 1 \times 10^5$  eV and radiation dose of  $5 \times 10^{13} - 1 \times 10^{18}$  ion/cm<sup>2</sup>.

The energy of these implanted ions is considerably higher than the energy of ions formed in the deposition chamber. These ions penetrate deep into the crystal lattice of the deposited metals or interstitial phases and cause changes in the interstitial element concentration, bring about formation of solid solutions and superstructural, non-stoichiometric compounds, and result in submicrostructure and strain modifications. All these result in improved adhesion strength and higher resistance of the coatings to erosion wear. Under the effect of such ion treatment, local temperature peaks may occur followed by rapid cooling of these surface localities, that results in the improvement of strength and tribological properties of the deposited microlayers.

Fig. 2 shows an exemplary X-ray pattern obtained from coatings deposited under various ion implant treatments in the deposition chamber; and Fig.3 shows the results of investigation by means of the Rutherford back scattering.

It is preferable to use a high energy pulsed ion source in order to reduce risks of overheating and temperature warping of a machine part under ion plasma deposition, which is especially important for aircraft engine compressor blades. Such source produces ions that have the energy high enough for the ions to be implanted into the crystal lattice of deposited phase and to create high-tensile compounds. The following rapid cooling of affected zones prevents the bulk material from overheating, causes the surface substructure to become finer and brings about nanocrystalline or amorphous structures in the surface microlayers.

5       The ion treatment improves, not only the resistance to erosion and corrosion,  
but also the endurance limit of machine components, especially under many-cycled  
fatigue conditions. The improvements are achieved due to the compressing strains  
generated in the interfacial boundaries and stable defects in the structure caused by the  
formation of fine precipitates of multiple-component metal/non-metal compounds of  
10   variable valence.

However, such complicated processes of multiple-layer coating deposition and  
ion implanted treatment may induce elevated internal stresses in the surface layers of  
machine components. In order that the stress distribution be favorable, it is necessary  
to carry out an additional treatment of the coated parts immediately after the  
15   deposition process. After the coated parts are unloaded from the deposition  
chamber, they are subjected to vibromechanical treatment with micro-pellets.

Therefore, the method claimed includes the following steps:

- (a) Preparing the surface for ion-plasma deposition.
- (b) Installing cathodes made of metals and alloys to be deposited.
- 20   (c) Placing workpieces or substrates into the ion plasma deposition chamber  
equipped with an ion implanter.
- (d) Ion beam cleaning of the surface.
- (e) Ion plasma depositing of coating comprising a plurality of microlayers with  
the required compositions and gas pressures in the deposition chamber.
- 25   (f) High-energy ion treatment of one or more microlayers during their  
deposition or after the coating has been deposited.
- (g) Cooling and unloading the workpieces.
- (h) Vibro-mechanical treatment according to the preset regime.

### 30       Brief Description of the Drawings and Photographs

Fig. 1 Microstructure of the wear-resistant coating on an aircraft engine blade of  
titanium-based alloy, x500x2;

Fig. 2 X-ray diffraction patterns from coatings with various implanted ions and  
35   regimes;

Fig.3 Results of investigation of coating by means of Rutherford back scattering;

Fig. 4 Erosion values represented by weight loss in testing conducted on gas-turbine  
engine compressor blades;

Fig. 5 Erosion values represented by chord wear in testing conducted on gas-turbine  
40   compressor blades;

- 5 Fig. 6 Fatigue test results obtained on test specimens and compressor blades with and without coating.

### Detailed Description of Preferred Embodiments

10 In practice, ion-plasma deposition of metal ions is carried out following the general principles of ion plasma deposition in a low pressure chamber from the corresponding metal cathode in an inert gas atmosphere, for instance, in argon or, in order to produce a nitride metal coating, in nitrogen, with a considerable potential difference between the hot cathode and a workpiece that plays a role of the anode.

15 The coatings listed in Table 1 were prepared as follows. Ion-plasma deposition and high-energy ion treatment were conducted in HHB-6.6 type of equipment with an ion implantor of "Pulsar" type, or an implantor with a non-heated cathode, equipped with high accuracy optical pyrometers and inert/non-inert gas feeding systems monitored to feed the gas atmosphere into the ion plasma deposition  
20 chamber and implantor.

Titanium, steel or nickel-based alloy aircraft engine compressor blades were first treated with high energy ion argon plasma at a potential difference up to 1,500 V between titanium cathode and the blades, to clean the blade airfoil surface from any solid, liquid or adsorbed gas impurities.

25 Let us consider in more detail the coating deposition embodiment designated as No. 8. After the blades of BT16 alloy were treated with abrasive liquid, washed and dried, the blades were then placed into the ion-plasma deposition chamber where they were subjected to ion cleaning in inert gas atmosphere and then they were coated with a plurality of microlayers, starting with the scandium submicrolayer.

30 The scandium submicrolayer of 0.3 - 0.8 micron in thickness was deposited on the blade airfoil surface, at a scandium cathode heating current of 10 - 200 A to provide a temperature of 200 - 400°C and a potential difference of 100 - 1,000 V between the blades and the scandium cathode. Titanium cathodes and zirconium cathode were not heated this time. The stage took approximately 2 minutes and the  
35 blades were rotated at 2.5 rpm. A titanium microlayer having a thickness of 0.6 - 1.6 microns was then deposited by inactivating the scandium cathode by switching off its source of current and heating the titanium cathode by applying a current of 20 - 200 A and a potential difference of 100 - 800 V between the anode and the blades under the

5 argon atmosphere. A temperature of the cathode up to 700°C was achieved over this stage. Then a titanium microlayer having a thickness of 1-2 microns was deposited under a nitrogen and argon atmosphere in the working chamber. Then pressure was increased and a microlayer of titanium nitride was formed of a thickness approximately 2 - 4 microns. The temperature of blades was maintained within 480 -  
10 550°C over the whole deposition process to prevent any phase transformation in the bulk material.

The titanium cathode was inactivated and zirconium cathode heated to the same temperature by the same current density and potential difference as for the preceding titanium deposition step. During the deposition of titanium nitride and  
15 zirconium nitride there was nitrogen implantation carried out. The aforesaid deposition steps were repeated several times in the same sequence in order to obtain the desired thickness of the coating.

In alternative embodiments the foregoing titanium and zirconium ion deposition steps may be repeated, substituted or interchanged with titanium nitride  
20 and/or zirconium nitride ion deposition steps carried out under a nitrogen atmosphere. Interchanging of different microlayers is provided by the alternating heating of the titanium or zirconium cathodes under an argon or nitrogen atmosphere. An example is shown in Fig. 3 of changes in composition of various microlayers of the coating deposited following the claimed method and analyzed by means of the Rutherford  
25 back scattering. Clearly, a desired total thickness of coating can be obtained from a plurality of microlayers, preferably 3 - 20.

In preferred embodiments, each or some of the microlayers of the full coating at different stages in its preparation may be subjected to high energy ions of argon, nitrogen, carbon, or boron as selected by control of the atmosphere in the ion  
30 implantor under a potential difference between the ion-implantor electrode and the blades of 10 - 50 kV.

Ion implantors are well-known in the art.

In the present embodiment, the ion implantor of "Pulsar" type is provided with a low pressure arc between a screened cathode spot and a widened anode part of the  
35 discharge. The arc provides a high current of non-metallic ions of argon or a non-inert gas medium injected into the implantor from the developed emission surface of the anode plasma. Cathode ion emission is negligible since the cathode is not heated. Further, on screening of the cathode spot prevents its interference with the anode

5 plasma and lowers contamination of the gas-discharging plasma by metallic ions. Accordingly, only ions from the arc anode plasma enter the ion optical system which forms the beam of high-energy ions. The plasma contains less than 0.1% of metal ions.

10 In the process according to the invention the following process parameters were used:

Accelerating voltage	up to 50 kV
Ion beam amperage: in impulse	1 A
average	50 mA
Beam cross-section: wide beam	150 cm <sup>2</sup>
15 convergent beam	5 cm <sup>2</sup>
Impulse duration	1×10 <sup>-3</sup> sec <sup>-1</sup>
Repetition rate	1 - 50 sec <sup>-1</sup>
Ion types - any gas ions, including ions of chemically active and inert gases	

20 A beam of nitrogen or boron or carbon or argon ions, emanating from an emitting electrode is accelerated through an accelerating electrode and an outlet electrode to intermittently impinge, as desired, on the individual microlayers of the substrate.

25 Table 1 gives the structural order and compositions of several examples of coated substrates according to the invention.

Table 1

Example No.	Substrate material	No. of microlayers in the coating	Total coating thickness (microns)	Material and order of coating
1	Titanium alloy	7	12-16	Sc,Ti+Zr,(Ti,Zr(N)), Zr,(Zr(N)), ZrN+Ar
2	Stainless steel	9	10-12	Sc,Ti+Zr,(Ti,Zr(N)), TiN+N,ZrN+N*
3	Titanium alloy	8	6-8	Ti,(Ti(N)),TiN, ZrN+N*
4	Nickel-based alloy	4	4-6	Y,Ti,(Ti(N)), TiN+Ar
5	Titanium alloy	17	14-18	Sc,Ti,(Ti(N)), TiN+N,Ti,+N,Zr,

				(Zr(N)), TiN, ZrN+N*
6	Nickel-based alloy	19	18-22	REM, Zr, (Zr(N)), ZrN, +Ar, Zr, (Zr(N))ZrN +Ar, Ti, (Ti(N)), TiN+Ar*
7	Titanium alloy	46	18-22	Sc, Ti, (Ti(N)), TiN, +N, Zr, (Zr(N)), ZrN, Ti, (Ti(N)), TiN+N, Ti, (Ti(N)), TiN+N, Zr, (Zr(N)), ZrN
8	Ti-6Al-4V alloy	19	14-18	Sc, Ti, (Ti(N)), TiN, +N, Zr, (Zr(N)), ZrN, +N, Ti, (Ti(N)), TiN*
9	Titanium alloy	25	28-32	Sc, Ti, (Ti(N)), TiN+NZr N+TiN, Zr+N, Ti, (Ti(N)), TiN+Ar
10	Titanium alloy	40	16-20	Cr, (Cr(C)), Cr <sub>3</sub> C <sub>2</sub> , ZrC+C, Zr, (Zr(C)), ZrC+C, ZrC, Zr, Cr <sub>3</sub> C <sub>2</sub> +ZrC*
11	Titanium alloy	57	14-18	Y, Ti, (Ti(C)), TiC+C, Ti, (Ti(C)), ZrC+C, Zr+C, Ti+C, ZrC, Ti, (Ti(C)), TiC+C, ZrC+Ti C, ZrC*
12	Titanium alloy	49	14-20	Y, Zr, (Zr(C)), ZrC+CZr, (Zr(C)), TiC+C, Ti Ti(C)), TiC+C, Zr, (Zr(C)), ZrC*

5

Note: +C,+N,+Ar - denote carbon, nitrogen or argon ion implant treatment respectively;

(Ti(N)), (ZrN)), (TiC), (ZrC), etc. - the microlayers comprising interstitial solid solutions of nitrogen and carbon in the corresponding metal;

10 \* - the microlayers are deposited in the specified order several times to obtain coating of desirable thickness;

Ti+Zr - the microlayer comprising of the mixture of the metals specified.

5

Fig.4 and Fig. 5 show erosion resistance of complex coatings comprising a plurality of microlayers produced, according to the invention, of zirconium, titanium and nitrides thereof, and subjected to erosion tests on Ti-6Al-4V alloy compressor blades with implanted nitrogen ions as compared to the non-coated blades. The Figures also specify the testing conditions.

Specified below is wear resistance test results, of coating specimens having the same number of microlayers and a total thickness of 12 - 16 microns with and without nitrogen or carbon implanted ions.

1. BT8 alloy (Ti-6Al-3.5Mo-0.5Zr) without coating = 1.0
2. Coating on BT8 alloy - Sc-Ti-(Ti(N))-TiN-Zr-(Zr(N))-ZrN = 0.12
3. Coating on BT8 alloy - Sc-Cr-(Cr(C)) - Cr<sub>2</sub>C<sub>3</sub>-(Zr(N))-ZrC = 0.26
4. Coating on BT8 alloy - Sc-Ti-(Ti(N))-TiN+N-Zr-(Zr(N))+N = 0.014
5. Coating on BT8 alloy - Sc-Cr-(Cr(C))- Cr<sub>2</sub>C<sub>3</sub>+C-Zr-(Zr(C))+C = 0.037

#### Testing conditions:

- Velocity of the air-abrasive flow - 120 m/sec
- Temperature - room temperature
- Abrasive material - quartz sand, of 10 microns granularity
- Abrasive material quantity - 10 kg
- Attack angle - 20°
- Specimens 4 and 5 are with implanted nitrogen and carbon ions, respectively
- Wear resistance was measured by weight loss as compared with non-coated specimens.



Corrosion tests

Coated as per the invention and non-coated steel and titanium blades were subjected to corrosion tests by the method as follows.

10 The titanium blades were heated at 300°C and the stainless steel blades at 420°C in a chamber for 1 hour. The blades were subsequently cooled in a 3% sodium chloride solution, held in a humid chamber for 23 hours and the cycle was repeated 10 times. These tests were meant to simulate 2 years of fan blade operation under conditions of humid tropical climate. Corrosion resistance evaluation was made by visual examination of the blades and vanes after each cycle and by determination of  
15 the change in mass during and after the corrosion tests.

The results showed that non-coated blades had a typical change in mass of 1.3g/m, in contrast to the coated blades which had no corrosion as measured visually neither any change in weight.

20 Another test was conducted in a chamber at 350°C in 3% sodium chloride solution vapors for 3 days. This test was meant to estimate pitting corrosion on the leading edge of the blades (to simulate corrosion conditions at moorings), and then the data obtained were averaged over 8 blades (see below):

1. Non-coated blades - over 20 pitting marks in the leading edge
2. Titanium nitride coated blades - 9-12 pitting marks
- 25 3. Blades coated with a plurality of microlayers and argon implanted according to the invention - 1 -3 pitting marks.

30 The comparison tests conducted on non-coated blades and the blades coated according to the invention have shown that the fatigue strength of the coated blades does not deteriorate and thus provides a high level of durability and high endurance limit (Fig.6). The fatigue test parameters were corresponding to the actual operating conditions of aircraft engine performance.

35 After the laboratory tests had been conducted, natural scale tests were performed on real engines, with abrasive material particles of 100 - 200 microns at the sand consumption rate of 1.2 kg/hour. These tests have also demonstrated a considerable improvement in erosion resistance of the aircraft compressor guide blades and rotor under severe conditions as compared to the non-coated blades. Fig.7 shows the surface of the blades. Therefore, the results obtained can be used to

- 5 develop a repair technology designed for improving durability of new blades of an aircraft engine.

Industrial applicability

- 10 The invention claimed can be used to improve durability and endurance limit of machine components by depositing wear and corrosion resistant coating on the component parts used in a variety of machine building industries, and to repair and restore component parts worn in operation. Particularly, positive results have been obtained for restoring worn-out compressor blades and for improving aircraft engine
- 15 compressor's durability and service life. Technologies based on the claimed invention can also be utilized in other industries, such as manufacture of consumer goods, domestic appliances, and sporting equipment.



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EXHIBIT B

5      **Method for Deposition of Wear Resistant Coatings to Improve Service Life of  
Coated Components**

Field of the Invention

10          This invention relates to metallurgy and machine building fields and more  
specifically to development of methods that improve service life and durability of  
machine components; to repair of components and reconstitution of their properties;  
and particularly to gas turbine blades and vanes; and primarily to coatings applied to  
metal surfaces of aircraft engine compressor blades and vanes.

15

Background of the Invention

Frequently, aircraft and helicopters equipped with gas-turbine engines have to  
operate under conditions of considerable dust content in the air flow and high  
20 humidity of sea environment with aggressive elements of corrosive effects. These  
operation conditions result in abrasion-caused erosion and corrosion of aircraft parts,  
particularly the compressor blades. Under these conditions, geometry of blades is  
distorted, operating performances are deteriorated, fuel consumption increases, and  
engine maintenance and repair expenses grow considerably. The said deteriorating  
25 processes can not be efficiently avoided by installation of dust protective devices.

Eroded blades and vanes are generally restored by edge profile polishing or are  
replaced with new blades and vanes. Such blades and vanes are made of titanium-  
based alloys or high-alloy steels, which are expensive and difficult to process, so  
engine repair entails great expense.

30          U.S. Patent No.4,904,542, issued February 27, 1990, reissued under Re.34,173  
on February 2, 1993, to Midwest Research Technologies Inc. describes a coating  
formed of a plurality of alternating layers of metallic and ceramic materials. The two  
materials selected for the layers have complementary wear resistant characteristics  
such that one is relatively ductile and the other is relatively hard and brittle.  
35 Preferably radio-frequency sputtering is employed to deposit the coating, since it does  
not produce excessive heating which could negate any prior heat treatment of the  
substrate onto which the coating is deposited.

5 Also known are RU Patents No.2,061,090 BI No. 15, 1996 and No.2,106,429 BI No. 7, 1998, that describe methods of multi-layer coating deposition on parts and tools, including transition metal coatings. Zirconium is offered as an adhesive bondcoat that is applied to the substrate before the coating; or there is an alternative method of applying metal oxides between the metal layers.

10 A deposition technique is also known to produce thin films of  $CN_x$  with implantation of nitrogen ions from plasma. U.S. Patent No. 5,580,429 issued December 3, 1996, to Northeastern University describes cathodic/anodic vacuum arc sources with a plasma ion implantation deposition system for depositing high quality thin film coatings on substrates. Both cathodic and anodic vacuum arc deposition  
15 sources, CAVAD, are used to create a plasma vapor from solid materials composing the cathode and/or anode in the cathodic and/or anodic arc, respectively. Gases, e.g., hydrogen or nitrogen can be in the deposited films by creating a background plasma of the desired gas using either RF energy, thermionic emission, or consequential ionization of the gas passing through the arc or around the substrate. Highly negative  
20 pulses are applied to the substrate to extract the ions and provide them with the appropriate energy to interact with the other species in the thin film formation on the substrate to form the desired films. The substrate is bombarded with ionized particles to form carbon nitrides with variable  $[N]/[C]$  ratios.

RU Patent No.2,062,818 issued June 27, 1996, describes deposition of metal-  
25 containing coatings on large substrates in vacuum. The method includes inert gas ion beam cleaning of the substrate and metal-coating deposition by cathodic sputtering in the inert gas discharge when the substrate is bombarded with the inert gas ion beam that is formed by an accelerator of closed-type drift of electrons at an inert gas ion energy of 50-150 eV. Technically, this method is the closest one to the present  
30 invention.

However, the aforesaid U.S.P. 4,904,542, U.S.P. 5,580,429 and R.U. 2,062,818, R.U. 2,061,090, and R.U. 2,106,429 do not fully cover the problems of durability and wear resistance, especially as far as aircraft engine blade airfoil surfaces are concerned, which must meet various specific requirements to their wear  
35 and corrosion resistance properties and at the same time retain a certain level of their mechanical and, particularly, fatigue characteristics.

Therefore, there is a need to provide improved erosion and corrosion resistance and, as a result, improved reliability and durability of components of

5 various machines, tools and equipment, especially gas turbine engine compressor blades and vanes. That is proposed to be achieved by vacuum plasma technology involving ion implantation.

### Summary of the Invention

10

It is an object of the present invention to provide a technique of coating deposition on metal surfaces, particularly on components of machines, steam and gas turbines, and even more specifically on aircraft engine compressor blades and vanes, that will ensure improved erosion and corrosion resistance and retain the sufficient level of mechanical properties, primarily, fatigue characteristics.

15 It is a further object to restore the metallic surface of an eroded or corroded metal substrate, particularly the profile surface of a working blade of a gas turbine engine compressor to its original geometric shape and profile parameters.

To achieve the aforementioned objects, a coating is deposited that consists of at least three or four microlayers with certain thickness and compositions. By the term "microlayer", in this specification and claims, is meant a layer of pure metal, multiple-component substitution or interstitial metal alloy with non-metal atoms, or interstitial phases based on the said metals, i.e. the metal carbides, nitrides, borides, or complex compounds of the said phases, e.g., carbonitrides, carboborides, etc..

25 The said coating is produced by means of ion plasma deposition; in the preferred embodiments, the said coating consists of a special microlayer (hereinafter referred to as "submicrolayer"); the said submicrolayer is a rare earth metal, particularly scandium, yttrium or lanthanum and lanthanoids; the said coating also comprises a plurality of microlayers wherein each of said microlayers comprises a material selected from the group consisting of the Group IV<sup>B</sup>~~A~~-VI<sup>B</sup>~~A~~ (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W) or alloys thereof, interstitial solid solutions of elements (carbon, nitrogen, boron), nitrides, carbides, or borides of metals, wherein one or more of said microlayers has been subjected to high energy non-metallic (argon, nitrogen, carbon, boron) ion deposition.

35 The said microlayers of metals or said alloys or metal/non-metal compounds deposited by means of deposition of ions or neutral particles under an appropriate inert gas or non-inert gas, such as nitrogen, methane, acetylene, diborane, should be deposited to a desired thickness, preferably 0.1-10 microns.

5       The microlayer may be an essentially discrete layer distinct from the adjacent  
 substrate or microlayers; or it may be a mixture therewith. Each of the microlayers  
 may comprise a pure metal or an alloy thereof as prepared, for example, if more than  
 one metallic cathode are simultaneously activated within the chamber or the cathodes  
 are made of alloys. The order of the plurality of microlayers can be selected by opting  
 10 between corresponding gas atmospheres in the working chamber and by activating the  
 appropriate cathode(s). The number and order of microlayers constituting the full  
 coating and the inert or non-inert gas ions deposition can be selected depending on  
 the specific requirements determined by the desired performances of machine parts or  
 the whole machine. For example, it is essential that guide blades of the aircraft engine  
 15 compressor had very hard and wear resistant surfaces, and at the same time fatigue  
 characteristics of the substrate alloy would not play a restrictive role, since such  
 blades are not subjected to high fatigue. On the contrary, working blades of the  
 compressor are very sensitive to fatigue conditions as such blades have to operate  
 under considerable fatigue stresses. Therefore, coatings designed for guide and  
 20 working blades differ in their thickness and number of microlayers.

The method claimed involves deposition of, at least, three functional microlayers:

1 - a damping, corrosion-resistant microlayer of a rare earth metal from the  
 Groups IV<sup>B</sup> - VI<sup>B</sup> or a replacement alloy based on said metals, deposited in inert gas  
 25 atmosphere to the desired thickness, preferably 0.02 - 5 microns, that provides  
 relaxation of erosion-caused stresses between solid layers and protects from  
 corrosion-aggressive agents of media;

2 - a reinforcing microlayer consisting of interstitial solid solutions of  
 nitrogen, boron, carbon in transition metals of the second layer, deposited to the  
 30 desired thickness, preferably 0.04 - 10 microns, in a non-inert gas (nitrogen, diborane,  
 methane, or acetylene, respectively, at a partial pressure of said gases  $0.05 - 5 \times 10^{-1}$  Pa)  
 atmosphere, that provides a gradual transition to a high strength layer;

3 - a wear-resistant, high strength microlayer consisting of interstitial phases  
 such as nitrides, borides, carbides or complex compounds thereof based on said  
 35 transition metals, deposited to the desired thickness, preferably 0.1 - 12.5 microns, in  
 corresponding non-inert gas atmospheres at a partial pressure of  $0.1 - 5 \times 10^{-1}$  Pa, that  
 provides resistance to erosion effects of abrasive particles.

5 The deposition of the aforementioned functional microlayers is carried out by activating the appropriate cathode made of a pure metal or a multiple-component alloy, by selecting the necessary partial pressure and composition of the gas atmosphere, and by controlling the appropriate time of deposition as required.

Fig. 1 shows an exemplary microstructure of the claimed coating on an aircraft engine compressor blade of titanium alloy.

Simultaneously, one or more microlayers is subjected to non-metallic (argon, nitrogen, carbon or boron) ion treatment by means of an ion implantor; it is important that such treatment must be carried out directly in the working chamber of the ion-plasma device, simultaneously with or immediately following the deposition process.

15 The ion treatment is carried out with ions at  $5 \times 10^3 - 1 \times 10^5$  eV and radiation dose of  $5 \times 10^{13} - 1 \times 10^{18}$  ion/cm<sup>2</sup>.

The energy of these implanted ions is considerably higher than the energy of ions formed in the deposition chamber. These ions penetrate deep into the crystal lattice of the deposited metals or interstitial phases and cause changes in the interstitial element concentration, bring about formation of solid solutions and superstructural, non-stoichiometric compounds, and result in submicrostructure and strain modifications. All these result in improved adhesion strength and higher resistance of the coatings to erosion wear. Under the effect of such ion treatment, local temperature peaks may occur followed by rapid cooling of these surface localities, that results in the improvement of strength and tribological properties of the deposited microlayers.

Fig. 2 shows an exemplary X-ray pattern obtained from coatings deposited under various ion implant treatments in the deposition chamber; and Fig.3 shows the results of investigation by means of the Rutherford back scattering.

30 It is preferable to use a high energy pulsed ion source in order to reduce risks of overheating and temperature warping of a machine part under ion plasma deposition, which is especially important for aircraft engine compressor blades. Such source produces ions that have the energy high enough for the ions to be implanted into the crystal lattice of deposited phase and to create high-tensile compounds. The following rapid cooling of affected zones prevents the bulk material from overheating, causes the surface substructure to become finer and brings about nanocrystalline or amorphous structures in the surface microlayers.



5       The ion treatment improves, not only the resistance to erosion and corrosion,  
but also the endurance limit of machine components, especially under many-cycled  
fatigue conditions. The improvements are achieved due to the compressing strains  
generated in the interfacial boundaries and stable defects in the structure caused by the  
formation of fine precipitates of multiple-component metal/non-metal compounds of  
10   variable valence.

However, such complicated processes of multiple-layer coating deposition and  
ion implanted treatment may induce elevated internal stresses in the surface layers of  
machine components. In order that the stress distribution be favorable, it is necessary  
to carry out an additional treatment of the coated parts immediately after the  
15   deposition process. After the coated parts are unloaded from the deposition  
chamber, they are subjected to vibromechanical treatment with micro-pellets.

Therefore, the method claimed includes the following steps:

- (a) Preparing the surface for ion-plasma deposition.
- (b) Installing cathodes made of metals and alloys to be deposited.
- 20   (c) Placing workpieces or substrates into the ion plasma deposition chamber  
equipped with an ion implanter.
- (d) Ion beam cleaning of the surface.
- (e) Ion plasma depositing of coating comprising a plurality of microlayers with  
the required compositions and gas pressures in the deposition chamber.
- 25   (f) High-energy ion treatment of one or more microlayers during their  
deposition or after the coating has been deposited.
- (g) Cooling and unloading the workpieces.
- (h) Vibro-mechanical treatment according to the preset regime.

#### 30       Brief Description of the Drawings and Photographs

Fig. 1 Microstructure of the wear-resistant coating on an aircraft engine blade of  
titanium-based alloy, x500x2;

Fig. 2 X-ray diffraction patterns from coatings with various implanted ions and  
35   regimes;

Fig.3 Results of investigation of coating by means of Rutherford back scattering;

Fig. 4 Erosion values represented by weight loss in testing conducted on gas-turbine  
engine compressor blades;

Fig. 5 Erosion values represented by chord wear in testing conducted on gas-turbine  
40   compressor blades;

- 5 Fig. 6 Fatigue test results obtained on test specimens and compressor blades with and without coating.

### Detailed Description of Preferred Embodiments

10 In practice, ion-plasma deposition of metal ions is carried out following the general principles of ion plasma deposition in a low pressure chamber from the corresponding metal cathode in an inert gas atmosphere, for instance, in argon or, in order to produce a nitride metal coating, in nitrogen, with a considerable potential difference between the hot cathode and a workpiece that plays a role of the anode.

15 The coatings listed in Table 1 were prepared as follows. Ion-plasma deposition and high-energy ion treatment were conducted in HHB-6.6 type of equipment with an ion implantor of "Pulsar" type, or an implantor with a non-heated cathode, equipped with high accuracy optical pyrometers and inert/non-inert gas feeding systems monitored to feed the gas atmosphere into the ion plasma deposition  
20 chamber and implantor.

Titanium, steel or nickel-based alloy aircraft engine compressor blades were first treated with high energy ion argon plasma at a potential difference up to 1,500 V between titanium cathode and the blades, to clean the blade airfoil surface from any solid, liquid or adsorbed gas impurities.

25 Let us consider in more detail the coating deposition embodiment designated as No. 8. After the blades of BT16 alloy were treated with abrasive liquid, washed and dried, the blades were then placed into the ion-plasma deposition chamber where they were subjected to ion cleaning in inert gas atmosphere and then they were coated with a plurality of microlayers, starting with the scandium submicrolayer.

30 The scandium submicrolayer of 0.3 - 0.8 micron in thickness was deposited on the blade airfoil surface, at a scandium cathode heating current of 10 - 200 A to provide a temperature of 200 - 400°C and a potential difference of 100 - 1,000 V between the blades and the scandium cathode. Titanium cathodes and zirconium cathode were not heated this time. The stage took approximately 2 minutes and the  
35 blades were rotated at 2.5 rpm. A titanium microlayer having a thickness of 0.6 - 1.6 microns was then deposited by inactivating the scandium cathode by switching off its source of current and heating the titanium cathode by applying a current of 20 - 200 A and a potential difference of 100 - 800 V between the anode and the blades under the

5 argon atmosphere. A temperature of the cathode up to 700°C was achieved over this stage. Then a titanium microlayer having a thickness of 1-2 microns was deposited under a nitrogen and argon atmosphere in the working chamber. Then pressure was increased and a microlayer of titanium nitride was formed of a thickness approximately 2 - 4 microns. The temperature of blades was maintained within 480 - 10 550°C over the whole deposition process to prevent any phase transformation in the bulk material.

The titanium cathode was inactivated and zirconium cathode heated to the same temperature by the same current density and potential difference as for the preceding titanium deposition step. During the deposition of titanium nitride and 15 zirconium nitride there was nitrogen implantation carried out. The aforesaid deposition steps were repeated several times in the same sequence in order to obtain the desired thickness of the coating.

In alternative embodiments the foregoing titanium and zirconium ion deposition steps may be repeated, substituted or interchanged with titanium nitride 20 and/or zirconium nitride ion deposition steps carried out under a nitrogen atmosphere. Interchanging of different microlayers is provided by the alternating heating of the titanium or zirconium cathodes under an argon or nitrogen atmosphere. An example is shown in Fig. 3 of changes in composition of various microlayers of the coating deposited following the claimed method and analyzed by means of the Rutherford 25 back scattering. Clearly, a desired total thickness of coating can be obtained from a plurality of microlayers, preferably 3 - 20.

In preferred embodiments, each or some of the microlayers of the full coating at different stages in its preparation may be subjected to high energy ions of argon, nitrogen, carbon, or boron as selected by control of the atmosphere in the ion 30 implantor under a potential difference between the ion-implantor electrode and the blades of 10 - 50 kV.

Ion implantors are well-known in the art.

In the present embodiment, the ion implantor of "Pulsar" type is provided with a low pressure arc between a screened cathode spot and a widened anode part of the 35 discharge. The arc provides a high current of non-metallic ions of argon or a non-inert gas medium injected into the implantor from the developed emission surface of the anode plasma. Cathode ion emission is negligible since the cathode is not heated. Further, on screening of the cathode spot prevents its interference with the anode

- 5 plasma and lowers contamination of the gas-discharging plasma by metallic ions. Accordingly, only ions from the arc anode plasma enter the ion optical system which forms the beam of high-energy ions. The plasma contains less than 0.1% of metal ions.

10 In the process according to the invention the following process parameters were used:

Accelerating voltage up to 50 kV

Ion beam amperage: in impulse 1 A

average 50 mA

Beam cross-section: wide beam 150 cm<sup>2</sup>

15 convergent beam 5 cm<sup>2</sup>

Impulse duration 1x10<sup>-3</sup> sec<sup>-1</sup>

Repetition rate 1 - 50 sec<sup>-1</sup>

Ion types - any gas ions, including ions of chemically active and inert gases

- 20 A beam of nitrogen or boron or carbon or argon ions, emanating from an emitting electrode is accelerated through an accelerating electrode and an outlet electrode to intermittently impinge, as desired, on the individual microlayers of the substrate.

25 Table 1 gives the structural order and compositions of several examples of coated substrates according to the invention.

Table 1

Example No.	Substrate material	No. of microlayers in the coating	Total coating thickness (microns)	Material and order of coating
1	Titanium alloy	7	12-16	Sc, Ti+Zr, (Ti, Zr(N)), Zr, (Zr(N)), ZrN+Ar
2	Stainless steel	9	10-12	Sc, Ti+Zr, (Ti, Zr(N)), <del>Ar</del> <del>Ti</del> N+N, ZrN+N*
3	Titanium alloy	8	6-8	Ti, (Ti(N)), TiN, ZrN+N*
4	Nickel-based alloy	4	4-6	Y, Ti, (Ti(N)), TiN+Ar
5	Titanium alloy	17	14-18	Sc, Ti, (Ti(N)), TiN+N, Ti, +N, Zr,

				(Zr(N)), TiN, ZrN+N*
6	Nickel-based alloy	19	18-22	REM, Zr, (Zr(N)), ZrN, +Ar, Zr, (Zr(N))ZrN +Ar, Ti, (Ti(N)), TiN+Ar*
7	Titanium alloy	46	18-22	Sc, Ti, (Ti(N)), TiN, +N, Zr, (Zr(N)), ZrN, Ti, (Ti(N)), TiN+N, Ti, (Ti(N)), TiN+N, Zr, (Zr(N)), ZrN
8	Ti-6Al-4V alloy	19	14-18	Sc, Ti, (Ti(N)), TiN, +N, Zr, (Zr(N)), ZrN, +N, Ti, (Ti(N)), TiN*
9	Titanium alloy	25	28-32	Sc, Ti, (Ti(N)), TiN+NZr N+TiN, Zr+N, Ti, (Ti(N)), TiN+Ar
10	Titanium alloy	40	16-20	Cr, (Cr(C)), Cr <sub>3</sub> C <sub>2</sub> , ZrC+C, Zr, (Zr(C)), ZrC+C, ZrC, Zr, Cr <sub>3</sub> C <sub>2</sub> +ZrC*
11	Titanium alloy	57	14-18	Y, Ti, (Ti(C)), TiC+C, Ti, <del>(Ti(C))</del> , ZrC+C, Zr+C, Ti+C, ZrC, Ti, (Ti(C)), TiC+C, ZrC+Ti C, ZrC*
12	Titanium alloy	49	14-20	Y, Zr, (Zr(C)), ZrC+CZr, <del>Zr(C))</del> , TiC+C, Ti Ti(C)), TiC+C, Zr, (Zr(C)), ZrC*

Note: +C, +N, +Ar - denote carbon, nitrogen or argon ion implant treatment respectively;

(Ti(N)), (ZrN)), (<sup>C</sup>Ti<sup>C</sup>), (<sup>C</sup>Zr<sup>C</sup>), etc. - the microlayers comprising interstitial solid solutions of nitrogen and carbon in the corresponding metal;

\* - the microlayers are deposited in the specified order several times to obtain coating of desirable thickness;

Ti+Zr - the microlayer comprising of the mixture of the metals specified.

5

Fig.4 and Fig. 5 show erosion resistance of complex coatings comprising a plurality of microlayers produced, according to the invention, of zirconium, titanium and nitrides thereof, and subjected to erosion tests on Ti-6Al-4V alloy compressor blades with implanted nitrogen ions as compared to the non-coated blades. The  
 10 Figures also specify the testing conditions.

Specified below is wear resistance test results, of coating specimens having the same number of microlayers and a total thickness of 12 - 16 microns with and without nitrogen or carbon implanted ions.

1. BT8 alloy (Ti-6Al-3.5Mo-0.5Zr) without coating = 1.0
- 15 2. Coating on BT8 alloy - Sc-Ti-(Ti(N))-TiN-Zr-(Zr(N))-ZrN = 0.12
3. Coating on BT8 alloy - Sc-Cr-(Cr(C)) - Cr<sub>2</sub>C<sub>3</sub>-(Zr(N))-ZrC = 0.26
4. Coating on BT8 alloy - Sc-Ti-(Ti(N))-TiN+N-Zr-(Zr(N))+N =  
0.014
- 20 5. Coating on BT8 alloy - Sc-Cr-(Cr(C))- Cr<sub>2</sub>C<sub>3</sub>+C-Zr-(Zr(C))+C =  
0.037

Testing conditions:

- Velocity of the air-abrasive flow - 120 m/sec
- 25 • Temperature - room temperature
- Abrasive material - quartz sand, of 10 microns granularity
- Abrasive material quantity - 10 kg
- Attack angle - 20°
- Specimens 4 and 5 are with implanted nitrogen and carbon ions,  
30 respectively
- Wear resistance was measured by weight loss as compared with non-coated specimens.

### Corrosion tests

Coated as per the invention and non-coated steel and titanium blades were subjected to corrosion tests by the method as follows.

10 The titanium blades were heated at 300°C and the stainless steel blades at 420°C in a chamber for 1 hour. The blades were subsequently cooled in a 3% sodium chloride solution, held in a humid chamber for 23 hours and the cycle was repeated 10 times. These tests were meant to simulate 2 years of fan blade operation under conditions of humid tropical climate. Corrosion resistance evaluation was made by visual examination of the blades and vanes after each cycle and by determination of  
15 the change in mass during and after the corrosion tests.

The results showed that non-coated blades had a typical change in mass of 1.3g/m, in contrast to the coated blades which had no corrosion as measured visually neither any change in weight.

20 Another test was conducted in a chamber at 350°C in 3% sodium chloride solution vapors for 3 days. This test was meant to estimate pitting corrosion on the leading edge of the blades (to simulate corrosion conditions at moorings), and then the data obtained were averaged over 8 blades (see below):

1. Non-coated blades - over 20 pitting marks in the leading edge
2. Titanium nitride coated blades - 9-12 pitting marks
- 25 3. Blades coated with a plurality of microlayers and argon implanted according to the invention - 1 -3 pitting marks.

The comparison tests conducted on non-coated blades and the blades coated according to the invention have shown that the fatigue strength of the coated blades  
30 does not deteriorate and thus provides a high level of durability and high endurance limit (Fig.6). The fatigue test parameters were corresponding to the actual operating conditions of aircraft engine performance.

After the laboratory tests had been conducted, natural scale tests were performed on real engines, with abrasive material particles of 100 - 200 microns at the  
35 sand consumption rate of 1.2 kg/hour. These tests have also demonstrated a considerable improvement in erosion resistance of the aircraft compressor guide blades and rotor under severe conditions as compared to the non-coated blades. Fig.7 shows the surface of the blades. Therefore, the results obtained can be used to

- 5 develop a repair technology designed for improving durability of new blades of an aircraft engine.

Industrial applicability

- 10 The invention claimed can be used to improve durability and endurance limit of machine components by depositing wear and corrosion resistant coating on the component parts used in a variety of machine building industries, and to repair and restore component parts worn in operation. Particularly, positive results have been obtained for restoring worn-out compressor blades and for improving aircraft engine
- 15 compressor's durability and service life. Technologies based on the claimed invention can also be utilized in other industries, such as manufacture of consumer goods, domestic appliances, and sporting equipment.